ECOTOXICOLOGICAL ANALYSIS OF GLASSES OBTAINED FROM FLY ASHES

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ABSTRACT

In this work a mixture design analysis was used to study the effect of coal ashes and galvanic, feldspar and fluorite residues in glassmaking. Five formulations with four factors at two levels were designed. The residues were dried, sieved, mixture according to the design and melted at 1,450°C during 2h for stabilization using 10wt% of $CaCO_3$ (fluxing agent). The melts were cast in a water-cooled mould and annealed (600°C) and the glasses were analyzed regarding their transition temperatures (Tg and Tm) by differential thermal analysis (DTA, air, 20°C/min) and biological effects by ecotoxicological tests (EN40). The results were analyzed by analysis of variance and plotted in response surfaces graphs in order to determine the individual influence of each residue in the studied properties. As a result, the melting temperature is strongly dependent on silica content of each glass, and the fluorite residue, being composed mainly by silica, strongly affects Tm. The ecotoxicological analysis shows the significant influence of the galvanic residue due to the high iron and zinc content of this waste.

1. INTRODUCTION

Ash produced from coal-fuelled power plants is much like volcanic ash. It consists of lime, iron, aluminium, silica sand, and clay, essentially materials from the Earth's crust, melted by the heat of combustion to form glass compounds. In addition, coal ash contains trace quantities (in the parts-per-million range) of the oxidized forms of other naturally occurring elements. These same elements exist in soil, rock and coal, as well as, trace elements that may include arsenic, boron, cadmium, chromium, copper, lead, selenium, and zinc [1,2].

Disposal and/or any use of coal ash are becoming a major issue because of its potential to contaminate surface and groundwater with arsenic, boron, heavy metals, etc. Knowledge of the chemistry of fly ash is essential in developing a methodology that can predict release rate(s) and concentration(s) of chemical constituents of environmental concern (pollutants). Safe disposal of fly ash with respect to surface and groundwater protection depends on having the know-how to evaluate the potential of a given fly ash to release toxic pollutants [6-9].

Coal ash is made of three types of solids: 1) chemically water stable solids (SiO, FeO, AIO), 2) relatively water soluble solids (metal-SO_4, metal-BO_3,), and 3) water reactive metal-oxides (CaO, MgO, K_2O, Na_2O, etc). Ash varies from acidic to alkaline because of the chemical make-up of the source coal. Physical appearance varies depending on coal type and furnace. All fly ash samples are mainly composed of glass-like porous beads that vary in chemical composition with respect to Al/Si/Fe ratio and pH from extremely low (pH near 3) to near pH 12. Alkaline fly ash is often associated with high boron levels and exhibits extremely low pH buffering capacity [1-3].

Because fly ash contains toxic elements, disposal sites should be monitored for excessive build-up of heavy metals, salts and alkalinity. Potential heavy metal problems with power plant wastes are greatly reduced by the pronounced liming effects of the wastes. A problem that some consider an environmental issue is the movement of heavy metals from fly ash in ponds or landfills to drainage waters. Levels of heavy metals or metalloids, e.g., selenium, chromium, boron, and in some instances, mercury and barium, exceeded the regulatory public water supply guidelines. Passage of the leachates through soil columns removed most of the dissolved elements. Thus, passage of pond effluents through soil was found to provide significant protection against ground water contamination. An important consideration is that soils that receive fly ash or ash disposal sites should always have the pH maintained at above 6 in order to keep most heavy metals immobile [1].

At present, hazardous fly ash is stabilized by incorporating it into cement-based materials. However cement-based techniques pose problems inside landfills due to weak chemical and physical stability. Particularly, in cases where fly ash with high concentrations of alkali chlorides, it is difficult to apply the cement-based techniques since the alkali chlorides inhibit hydration of cement so that the cement matrix cannot be fully solidified or stabilized [4-8].

Therefore, it is necessary to search for new techniques for treatment of fly ash. Vitrification is one of the most promising solutions among the various available technologies. Furthermore, toxic organic compounds such as dioxins can be destroyed during the vitrification process. There are several reports on the vitrification of solid waste [8-13]. It was demonstrated that the addition of bottom ash and glass wastes into fly ash facilitated the formation of glasses upon melting and quenching.

One relevant point is how to determine if any material or product made by fly ashes – or other residues – is really inert or stable. The regular standards (EN 13657:2002; EN 14735:2005; ISO 11932:1996; ISO 17616:2008 and others) try to determine if a solid material is toxic or not based on solubility, leachability and ecotoxicological tests, but there is no regulatory ecotoxicity testing and test methodology for waste materials. Several main issues have emerged including: (i) methods of dispersion and whether or not ecotoxicity tests should use dispersed solid wastes; (ii) the chemical characterization of the test material; (iii) reference materials for regulatory ecotoxicology; (iv) modifications to test methods or solution preparation that enable existing regulatory ecotoxicity tests to work with waste materials; (v) triggers for conducting the tests, and whether or not new tests are needed, or additional measurements within existing tests, to quantify novel or unusual toxicological properties. Therefore, there is an opportunity in this new area of ecotoxicology to set the standards for chemical and ecotoxicological characterization of waste materials for fundamental research, as well as for regulatory toxicity testing [14-17].

The aim of this work was to determine the effectiveness of the vitrification technique in the stability of glasses obtained from fly ashes and mineral and galvanization residues through an ecotoxicological test. A mixture design was used to determine the influence of each residue in the stability of the glass system, and two micro-organisms were used in the ecotoxicological tests, *Escherichia coli* and *Staphylococcus aureus*, by the agar diffusion test.

2. EXPERIMENTAL PROCEDURE

Dry bottom ashes from Tractebel Energia S.A. thermoelectrical powerplant (Capivari de Baixo, Brazil) were vitrified with feldspar, fluorite and galvanization residues. All residues were analyzed by X-ray fluorescence spectroscopy (XRF, Philips PW2400, molten sample), table 1. The vitrification of the residues was performed with 10% Na_2CO_3 addition at 1450°C for 2 h, in air, in a chamber furnace using alumina crucibles. The resulting glasses were dark brown.

residue	SiO_2	Al_2O_3	Fe_2O_3	K_2O	TiO_2	MgO	Na_2O	CaO	F	Zn	Cl	SO_3	LOI
coal ash fluorite	69.0	24.8	1.9	1.9	1.1	0.3	0.2	0.2	-	-	-	-	0.3
fluorite	80.0	9.7	1.6	3.3	0.4	0.3	0.6	0.9	0.9	-	-	0.2	1.7
galvanic	1.2	0.2	19.9	-	-	-	-	9.3	4.1	9.4	14.0	0.3	41.3
feldspar	73.5	16.3	1.3	2.2	0.1	0.3	3.3	1.0	-	-	-	-	0.9

Table 1. Chemical analysis of the residues.

Five formulations with four factors at two levels were designed. The residues were dried, sieved, mixture according the design and melted at 1450°C during 2h for stabilization. The melts were quenched in a water-cooled mould and annealed at 600°C in a muffled furnace. Ash, galvanic mud, fluorite residue and feldspar residue were the factors and their amounts in each glass were the levels, as shown in table 2. The composition 5C represents the central point of the design and the others (V) represent the vertices.

comp. [%]	fly ash	feldspar	fluorite	galvanic mud	EC [mm]	SA [mm]
1V	20	30	20	30	0.0	0.0
2V	20	30	40	10	0.0	0.0
3V	20	50	20	10	0.0	0.0
4V	40	30	20	10	0.0	1.6
5C	25	35	25	15	1.8	2.9

Table 2. Mixture design for the vitrification process.

The powdered glass materials shown in table 2 (samples 1 to 5) were subjected to microbiological analysis to evaluate their inertness (stability). The Agar Diffusion Test was used for each sample and applied to *Escherichia coli* and *Staphylococcus aureus* bacteria (respectively EC and SA on table 2), according the following procedure: Bacterial cells from pre-inoculation (PDA medium plates – Petri dishes) grown for 16 hours were screened in new plates containing the same medium. One plate was produced for each bacterial species and two samples of each glass material were added in circles of 1.1 cm in diameter on the surface of it. The plates were incubated to 37°C for 24 hours and then photographed (digital camera) in order to measure the total diameter of the inhibition halos, expressed as mean diameters (two samples per glass composition).

3. RESULTS AND DISCUSSION

The chemical analysis of the residues is shown in table 1: the ash, feldspar and fluorite residues have similar composition with relatively high contents of SiO_2, Al_2O_3 and alkaline oxides; the galvanic residue has mainly Fe_2O_3, CaO and halogens, with a high loss on ignition.

Table 3 presents the analysis of variance (ANOVA) for the Agar Diffusion Test applied to *Escherichia coli* bacteria for the mixture design. The analysis shows no statistical significance, given by the F value (~0). An **F-test** is any statistical test in which the test statistic has an F-distribution if the null hypothesis is true. It is most often used when comparing statistical models that have been fitted to a data set, in order to identify the model that best fits the population from which the data were sampled. Exact F-tests mainly arise when the models have been fitted to the data using least squares.

The **p-value** is the probability of obtaining a result at least as extreme as the one that was actually observed, assuming that the null hypothesis is true. The fact that p-values are based on this assumption is crucial to their correct interpretation. The lower the p-value, the less likely the result, so the more "significant" the result, assuming the null hypothesis in the sense of statistical significance. The p-values are often used as 0.05 or 0.01, corresponding to a 5% chance or 1% of an outcome that extreme, given the null hypothesis. Since the p-value for the EC Agar Diffusion Test is near 1, the results have no statistical significance (EC, table 2), and could not be analyzed in this study.

model	SS_{efect}	dF_{efect}	MS_{efect}	SS_{error}	dF_{error}	MS_{error}	F	p	R^2
lineaR	0.00112	3	0.00037	2.65	1	2.65	0.00014	0.999	0.00042
total	2.65	4	0.66						

SS=sum of squares; dF=degree of freedom; MS=mean squares.
Table 3. ANOVA for the Agar Diffusion Test for the glass system using Escherichia coli bacteria (diameter of the inhibition halos, in mm).

Figure 1 shows the inhibition halos for the Agar Diffusion Test. The figure shows the Petri dishes for all samples, after the pre-inoculation with the *Escherichia coli* bacteria and incubation (24h, 37°C) with each glass. Besides the ANOVA results having no statistical significance, table 3, there is no inhibition halos for samples 1 to 4, meaning that the glass samples are inert for the EC bacteria, i.e., they are chemically stable and the vitrification process was efficient. Sample 5, presenting a 1.8mm halo, is the central point of the mixture design, with 25wt% of fly ash and 15wt% of galvanic residue. The results indicate that there is a critical SiO_2/Al_2O_3 ratio to prevent the glasses from being toxic to the micro-organisms used in this study. Besides the galvanic mud and the fluorite residue being clearly toxic, table 1, if there are sufficient glass formers and stabilizers, given by the SiO_2/Al_2O_3

ratio, these residues became inert by vitrification. When the SiO_2/Al_2O_3 ratio is not adequate, sample 5, the glass became non-inert.

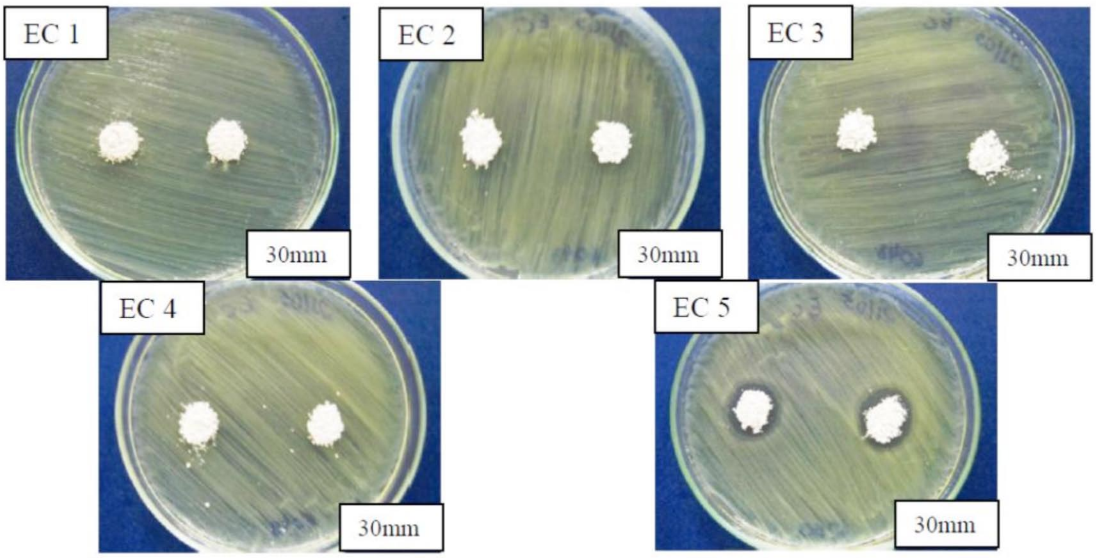

Figure 1. Inhibition halos for the Agar Diffusion Test using Escherichia coli for the glass system.

It should be observed that several standard ecotoxicological tests use other micro-organisms, as *Daphnia magna* and *Vibrio fischeri*, as indicators that a substance or material is not inert and can change the environment. The use of *Escherichia coli* and *Staphylococcus aureus* in this work is due the ease of the Agar Diffusion Test procedures, in comparison with other tests [18, 19].

Table 4 presents the analysis of variance (ANOVA) for the Agar Diffusion Test applied to *Staphylococcus aureus* bacteria for the mixture design. The analysis of variance also shows no statistical significance, given by the F-value (~0) and p-value (~1).

model	SS_{efect}	dF_{efect}	MS_{efect}	SS_{error}	dF_{error}	MS_{error}	F	p	R^2
linear	1.835	3	0.611	4.895	1	4.89	0.125	0.934	0.273
total	6.725	4	1.68						

SS=sum of squares; dF=degree of freedom; MS=mean squares.
Table 4. ANOVA for the Agar Diffusion Test for the glass system using Staphylococcus aureus (diameter of the inhibition halos, in mm).

Once again, since the p-value for the SA Agar Diffusion Test is near 1, the results have no statistical significance (SA, table 2), and could not be analyzed in this study. The same comments made for the tests with the EC bacteria shall apply for the tests with the SA, the samples being more aggressive for this bacterium, a Gram-positive bacterium, i.e., meaning that it can produce "coagulase", a protein product, which is an enzyme that causes clot formation. Figure 2 shows the inhibition halos for the *Staphylococcus aureus* Agar Diffusion Test.

The glass structure is usually considered as a random network. The elements are generally classified into three types: (1) network forming atoms: such as Si, B, P, Ge; (2) network modifiers (or glass fluxes): such as Na, K, Li, Ca, Mg; and (3) intermediates: such as Al, Fe, Zn, Ti, and Mo. The glass structure is mainly influenced by the glass composition. The components that form the strongest bonds in glasses result in the greatest improvement to the glass stability, whereas those that form the weakest bonds generally prove the greatest detriment to glass stability, i.e., the glass tends to be non-inert [13].

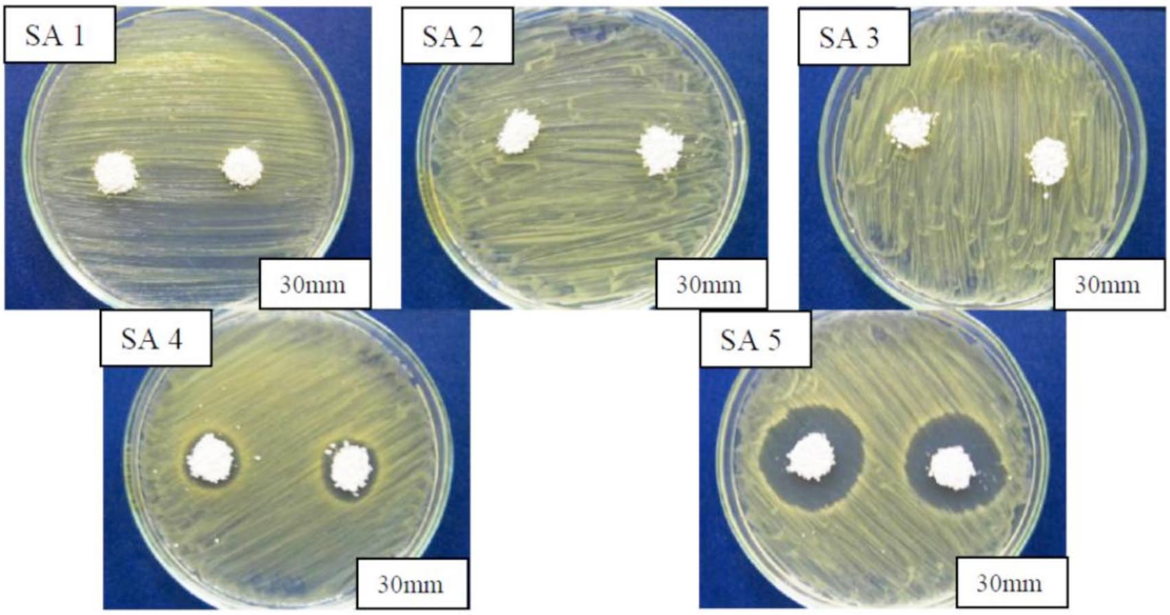

Figure 2. Inhibition halos for the Agar Diffusion Test using Staphylococcus aureus or the glass system.

Adding SiO_2, Al_2O_3, B_2O_3, and ZrO_2 may improve these properties; and adding alkali metal oxides may decrease them. If the inorganic oxides from the waste have insufficient glass formers to fall within an accepted glass formulation range, additional glass formers must be added through the process. According to current knowledge, if the coal fly ash does not contain proper ratios of materials for the formation of a glass, additives may be needed. The coal fly ash contains high contents of SiO_2 and Al_2O_3, but has insufficient glass network modifiers. Although the network modifiers (such as alkali metals) may decrease the glass properties, they are important to control the melted glass viscosity and thermal behaviour. The most effective glass modifier is Na_2O. In contrast to CaO or MgO, adding Na_2O will not increase the crystalline tendency. From an economic viewpoint, fewer kinds of additives are also desirable [12].

Therefore, the galvanic residue, owing to its content in Fe and Zn oxides, is more suitable for obtaining stronger glasses at high melting temperatures because it forms higher bond energies when compared with the alkaline and earth-alkaline residues. Also, it acts as a nucleating agent promoting the devitrification of the glass system, but this feature was not studied in this previous work. Finally, the vitrification of solid wastes is a well-known process used to immobilize hazardous elements, and the biological tests carried out to determine the toxicity of the glass system show this feature.

4. CONCLUSION

The mixture design is useful to determine which residue is able to form glasses with high or low melting temperatures and good mechanical properties. The waste vitrification in order to obtain low cost and common glasses is a well-known mechanism to immobilize hazardous elements and to transform them into glass-ceramics containing crystalline phases with high chemical and mechanical properties.

The thermoelectrical bottom ash belongs to the Si-Al-Fe system and so it is easily capable to give glass. In order to decrease the viscosity of the melts (visible as a lowering of the glass transition temperature in DTA) it is necessary to increase the Na_2O content. Also, the presence of Fe_2O_3 and ZnO in the galvanic residue results in higher bond energies in the glass structure and promotes a devitrification process with the transformation of these amorphous materials into the corresponding glass-ceramics product, not explored in this previous work.

Finally, the vitrification of solid wastes is a well-known process used to immobilize hazardous elements, and the ecotoxicological tests carried out in this study show that there is a critical SiO_2/Al_2O_3 ratio to prevent the glasses from being toxic to a given micro-organism.

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